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REINFORCING OF THERMOPLASTIC POLYCARBONATE AND POLYSULFONE WITH CARBON FIBERS--PRODUCTION AND CHARACTERISTICS OF UD-COMPOUND OBJECTS

E. Fitzer and H. Jaeger

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16. Abstract
The production and characteristics of the carbon fiber-reinforced thermoplastics polycarbonate and polysulfone are described. The production of prepregs from defined polymer solutions is emphasized along with methods of optimizing the production of compounds. The characteristics of unidirectionally reinforced thermoplastics, such as shear strength, bending strength, and impact resistance are compared with regard to fracture behavior, the influence of intermediate layers, and the behavior under cryogenic conditions nad under slightly elevated temperatures. The problem of adhesion between high-strength carbon fibers and thermoplastics is examined, taking into account the effect of moisture on the shear strength and the impact resistance.

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REINFORCEMENT OF POLYCARBONATE AND POLYSULFONE THERMOPLASTICS WITH CARBON FIBERS: PRODUCTION AND PROPERTIES OF THE UNIDIRECTIONAL COMPOSITES

E. Fitzer, H. Jäger

Introduction of carbon-fiber-reinforced thermoplastics has / 1
supplemented the previous range of application of carbon-fiber-reinforced thermosetting plastics such as epoxy resins and polyimides in air and space transport. More importantly, it has opened up other new areas of application. This study describes production and properties of carbon-fiber-reinforced polycarbonate (PC) and polysulfone (PSU) thermoplastics. It considers especially the production of prepregs from defined polymer solutions and optimization of the process for making the composites. This process can be aplied to carbon fiber types. The properties of the two unidirectionally reinforced thermoplastics such as interlaminar shear strength (ILSS), bending strength and impact resistance are discussed comparatively with respect to fracture behavior, effect if intermediate layers, and behavior at cryogenic and moderately elevated temperatures. The problem of adhesion between high-strength carbon fibers and thermoplastics is particularly discussed in relation to the effect of humidity on ILSS.

1. Introduction

Thermoplastics can be fiber-reinforced by short or endless fibers. When the composite is stressed, the stress between fibers and matrix is constant over the whole length, while with short-fiber reinforcement the maximum value is only reached with increasing distance from the fiber end toward the fiber center [1]. A minimum fiber length, the so-called critical length, is needed for this.

1.1 Short fiber reinforcement

Up to the end of the 1970s, thermoplastics were reinforced only with short fibers. In tests with short fiber lengths between 0.3 and 1.9 mm, the best mechanical properties of composites were found at 0.6 mm [2-5]. Fiber reinforcements with fiber lengths less than the critical length led to failure of the composite within the matrix or in the fiber/matrix boundary region [6-8]. When the critical fiber length was exceeded, the fracture of the composite was initiated within the fibers.

The fiber diameter also affected the composite properties. Best results, according to Mallick [7], were obtained with a ratio of fiber length to fiber diameter of 50 to 125.

The stress transferred to the fiber along the fiber length depends not only on the specific fiber properties but also, although to a lesse extent, on the deformation behavior of the matrix. Thus both parameters affect the value of the critical fiber length.

But the critical fiber length depends most strongly on the volume content of fibers. From calculations of the composite properties for an ideal plastic matrix on one hand [8] and an elastic matrix on the other hand [9], one arrives at the same result for the critical length of short glass fibers, i. e., 0.2 mm for a fiber content of 10% by volume, with an increase of the critical fiber length to 1 mm at low fiber content and a reduction of the critical fiber length to 0.05 mm at fiber volume proportions greater than 10%.

1.2 Effect of the fiber material in reinforcement with short and endless fibers

The expected effect of the fiber material on the composite properties was investigated comparatively by Harnier [10] with glass and carbon fibers. The expected higher stiffness of the carbon-fiber-reinforced composites was demonstrated. In earlier investigations, Ogorkiewic [59] could not detect a clear advantage of carbon fibers for short fiber reinforcement, but showed that carbon fibers with lengths greater than 50 mm, or, better, long carbon fibers, would have to be used to reach higher composite strengths and moduli.

Buhl [11] in 1980 summarized as follows the significant advantages of carbon-fiber-reinforcement of thermoplastics, as compared with other fibers:

- higher E-modulus at lower density
- higher use temperature
- lower coefficient of expansion
- higher damping
- lower tendency to creep
- lower specific electrical resistance.

1.3 Fiber/matrix adhesion

The great advance in composite technology first succeeded in the 1950s with the directed introduction of adhesion promoters in the form of silanes. The mechanism of action of such a 'finish' is not due only to improved adhesion, but also to reduction of sensitivity to humidity for both the glass fiber and the thermoplastic composite.

The importance of adhesion between fibers and matrix with glass fiber reinforcement as the example was shown first [12,13]. Good adhesion promoters for thermoplastics are peroxide groups and unsaturated bonds to the Si atom [14]. For glass fiber reinforcement of polypropylene, polyazide formates and azide formates have been discussed as functional silane adhesion promoters [15]. Cationic styryl silane is a particularly hydrolysis-resistant adhesion promoter for thermoplastics. Its action can still be increased by peroxide pretreatment [16-18]. Other / 2
literature on the importance of adhesion promotion in thermoplastics reinforced with short glass fibers appear in references [19 - 22].

1.4 Fiber content in the composite

Fiber contents up to 65 % by volume are common for endless fiber reinforcement in unidirectional laminates, while contents are only between 20 and 50 % by volume with short fiber reinforcement of thermoplastics [19]. The mechanical properties of the composites increase with increasing volume proportion (see data on reinforcement of nylon-6 and polycarbonate [23].) Fiber contents up to 60% by volume can be attained with short fibers only with strong preorientation, simultaneously approaching the anisotropy of the mechanical composite properties of unidirectional laminates.

The effect of the short fiber volume proportion on the impact resistance of composites is not uniform. A linear increase with fiber content is described for the thermoplastics polycarbonate, nylon-6 and nylon-6,6, while a maximum in impact strength is reached at 30% by volume for nonreactive thermoplastics [2]. The disadvantage of the impact sensitivity of carbon-fiber-reinforced thermoplastics will be mentioned later (section 9, p. 12).

1.5 Production methods

The industrial penetration of reinforced thermoplastics succeeded due to introduction of new working methods which allowed working with endless fibers in these matrix systems also. For polysulfone, a 2-stage process (prepreg production through dissolving the polysulfone in a suitable solvent and then pressing at suitable press temperature and pressure [24,25]). A pressure-infiltration method [25] has also been described.

Brownbill [26] describes the newest important prepreg technologies for carbon- and glass-fiber-reinforced thermoplastics, which are coming into use in thermoplastic reinforcement.

Aside from the advantage of sample composite production, one must mention the possibilities for simple thermal post-shaping (reforming), supplemental welding, high surface quality and low susceptibility to hydrolysis.

1.6 On application of fiber-reinforced thermoplastics

Cluley [17] has reported on the use of nylon-6, polysulfone (PSU) and polyether-ether-ketone (PEEK) (long-fiber-reinforced) as matrices for load-bearing parts. Potential applications open up in air and space transport for PSU and PEEK in particular because of their higher thermal resistance.

A comparative consideration of modern thermoplastics with respect to their structure (amorphous or crystalline) by Humphris [28] shows that crystalline thermoplastics exhibit better chemical resistance than amorphous systems, while amorphous thermoplastics have higher resistance to thermal deformation.

Because of the biocompatibility of PSU and carbon fibers, biological application is a potential along with industrial applications. For low-temperature applications, use of polycarbonate and polysulfone is discussed [29, 30]. They are superior to the usual duroplasts because of their extremely high elasticity in temperature ranges down to

4.2 Kelvin. Later works [31-35] have reported on future introduction of the thermoplatic PEEK, which is highly resistant to thermal deformation and t chemicals. This expands the spectrum of quite varied applications which cannot be covered with the existing thermoplastic matrices. The possibility of variations of properties not only through modification of the plastic matrix but also of the reinforcing components thus contributes to the expansion of plastic composites into areas in which metallic materials have dominated.

1.7 Content of this experimental study

The following study presents experimental results on prepreg production and measurements on unidimensional (UD) composites with polycarbonate (PC) and polysulfone (PSU) as the matrices. The properties of composites from carbon-fiber-reinforced thermoplastics PC and PSU are compared experimentally. The influence of the fiber/matrix adhesion is clarified by suitable selection of the state of surface treatment of the carbon reinforcing fibers. Application of adhesion-promoting intermediate layers is described as a possibility for improving these properties. Furthermore, the effect of test temperature on the mechanical properties of the composites are shown.

It is well known that the unfavorable impact strength behavior and susceptibility to humidity decisively limit the practical applications of such advanced composites. Therefore, the behavior of the composites under these more severe test conditions is described.

2. Characterization of the starting materials

2.1 On the viscosity of the matrix polymers

No special infiltration or curing problems appear in production of advanced composites with reactive resin matrices such as epoxides, principally because of the low viscosities of these resin compositions.

Figure 1 (left half) shows, for instance, the viscosity behavior of a commercial epoxy resin mixed with the stoichiometric amount of a diamine hardener (both resin components from Ciba-Geigy) and the temperature rise due to the exothermic cross-linking reaction as functions of the mixing time.

One can clearly recognize the reduction of the viscosity after a mixing time of 20-30 minutes, followed by a strong increase in viscosity with increasing temperature of the mixture. This strong increase in viscosity is caused by cross-linking reactions between the individual epoxides and diamines. In each case, though, the viscosity of the mixture in the liquid state is lower than that of the molten thermoplastics, polycarbonate and polysulfone (Figure 1, right half). As a result, processing of these thermoplastic systems is significantly more difficult than for the expoxy resin mixtures. Only above 220 °C in the case of the polycarbonates and above 300 °C for polysulfone are their viscosities reduced to the extent that / 3
processing at high pressures appears possible.

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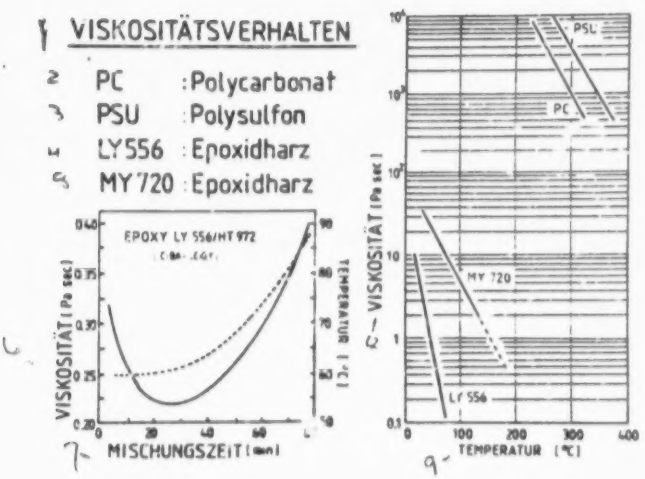

Figure 1. Effect of the cross-linking reaction in the curing process of the epoxy resin LY 556 with diamine HT 972 on the viscosity and temperature of the mixture (left half of figure), and comparison of the viscosities of epoxides with those of the thermoplastics PC and PSU vs. temperature.

1. Viscosity behavior
2. PC : Polycarbonate
3. PSU : Polysulfone
4. LY556 : Epoxy resin
5. MY720 : Epoxy resin
6. Viscosity
7. Mixing time
8. Viscosity
9. Temperature

Nevertheless, good ability to infiltrate the fiber strands remains in question. Better infiltrability can be expected for solutions of these thermoplastics in suitable solvents.

2.2 The thermoplastics used

The molecular structures and mechanical properties of polycarbonate and polysulfone are shown in Figure 2. The polysulfone shows somewhat higher bending strength and E modulus, while the polycarbonate has about 10% greater breaking elongation. Both thermoplastics have a large number of polar groups. For instance, the individual units of the polysulfone are linked through ether and SO_2 groups. The polar links in the polycarbonate are less stable to hydrolysis, though.

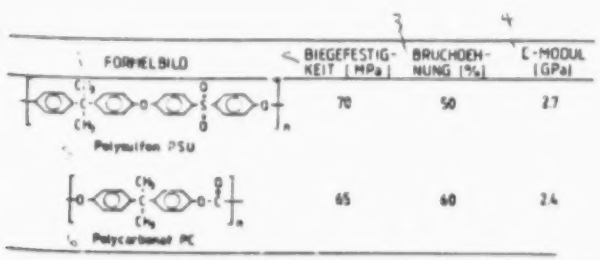

Figure 2. Structure and mechanical properties of the thermoplastics PSU and PC.

1. Structural formula
2. Bending strength [MPa]
3. Elongation [%]
4. E-modulus [GPa]
5. Polysulfone PSU
6. Polycarbonate PC

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Neither matrix has potential for reaction with surface groups of the carbon fiber. Therefore, bonding is possible only through dipole interactions between the individual reactive components on both the fiber and the matrix and through hydrogen bonds. Decisive weakening of these bonds can be expected through accumulation of water at the carbon fiber surface due to the reduction of the dipolar character of the fiber surface which that causes.

2.3 The carbon reinforcing fibers used

Both high-strength (Hercules AS4, Torayca T 300, Toho HT A7) and high-modulus (Torayca M 40, Sigraphil HM 12) types of carbon fibers were used to reinforce these matrix materials.

As apparent from Table 1, the significant differences between the high-strength and high-modulus types are in the E-modulus and breaking elongation.

Table 1. MECHANICAL PROPERTIES OF THE HIGH-STRENGTH (HF) AND HIGH-MODULUS (HM) CARBON FIBERS USED IN THE STUDY.

Type	Fiber	E-modulus GPa	Tensile strength MPa	Breaking Elongation %
HF-C	HERCULES AS 4	250	4500	1.6
	TORAYCA T 300	230	3500	1.3
	TOHO HTA 7	230	3400	1.4
HM-C	TORAYCA M 40	390	2700	0.7
	SIGRAFIL HM 12	350	2000	0.5

3. Preliminary tests on laminate (prepreg) production

There are two possibilities for prepreg production:

i) discontinuous laminate production by immersion of a dry pre-wound shape in a polymer solution of definite composition for a definite residence time.

ii) contnuous impregnation of a carbon fiber strand in solutions with defined thermoplastic content for defined residence times and wet-winding these strands into laminates.

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3.1 Discontinuous prepreg production

First, the infiltration behavior of the carbon fiber strands was investigated as a function of the residence time in the solution, with a definite polymer content in the solution (here 10% polycarbonate in CH_2Cl_2).

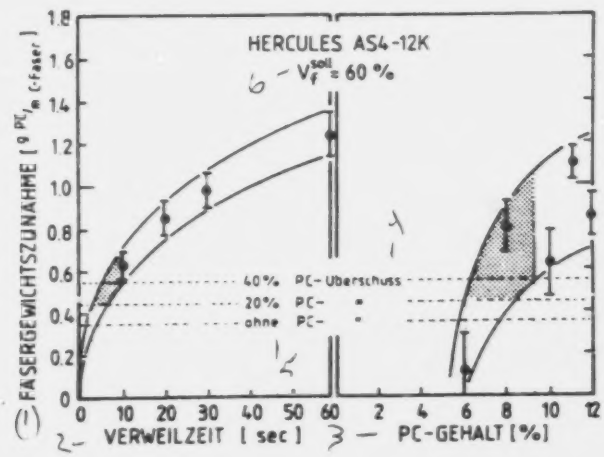

Figure 3. Fiber weight increase due to PC with extended residence time in the PC solution, and weight increase with increasing concentration of PC solution.

1. Increase in fiber weight [g PC/m of fiber]
2. Residence time [sec]
3. PC content [%]
4. excess
5. without
6. intended V_f = 60%

As shown by the increase in fiber weight after drying in Figure 3, unmixing has occurred in the solution, so that the thermoplastic (here, polycarbonate) is enriched on the fibers and depleted in the solution. At 10 seconds residence time in a 9 - 10% polycarbonate solution in CH_2Cl_2 the polycarbonate proportion of 48 - 52% is achieved in the prepreg before further processing. This corresponds to a 20-30% excess of polymer, compared to the proportion of the polymer in the finished composite. This is required to assure the possibility of processing the prepreg to make a finished nonporous end product. The results in Figure 3 refer to the Hercules AS 4-12 carbon fiber. The applicability of the results to other fiber types must be tested experimentally in each case (cf. Figure 4). /4

3.2 Continuous prepreg production

In the preliminary experiments on continuous impregnation with defined thermplastic solutions the residence time of the fiber strand to be impregnated within these solutions was varied so that the dried fiber would be loaded with about 20% excess of thermoplastic.

One can see from Figure 4 that the degree of polymer deposition depends on both the concentration of the polymer solution and the type of carbon fiber. For the fiber Hercules AS 4 one needs a solution of 7% polysulfone in CH_2Cl_2, but a 10-11% polycarbonate solution. Torayca T300 used in place of Hercules AS 4 even needs a 12% polysulfone solution.

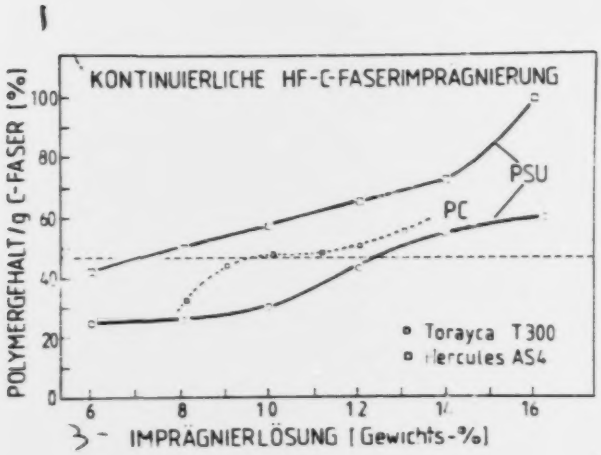

Figure 4. Polymer deposition on carbon fibers, as affected by fiber type and polymer concentration.

1. Continuous high-strength carbon fiber impregnation
2. Polymer content/g Carbon fiber [%]
3. Impregnating solution [weight %]

3.3 Preliminary experiments on accumulation of water on carbon fibers

Figure 5 shows water accumulation on the Hercules AS 4 carbon fiber by means of the weight increase on storage in a medium with a relative humidity of 63.5% at 26.5°C.

The steep initial rise in weight can be explained as due to rapid monomolecular covering of the individual monofilaments with water. The slow reduction in this adsorption is due to the decrease in surface polarity with multilayer coating due to the previous monolayer formation.

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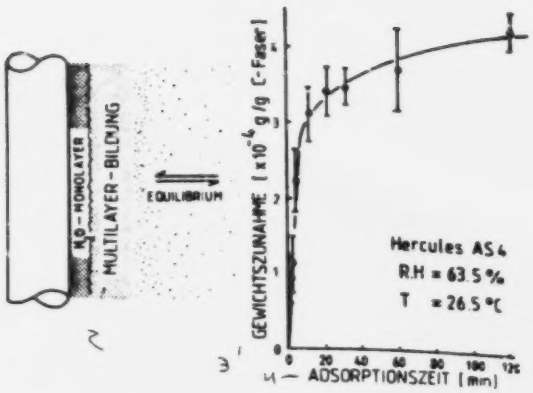

Figure 5. Adsorption of water from the air on the carbon fiber Hercules AS 4.

1. Water adsorption on the carbon fiber surface
2. Multilayer formation
3. Weight increase [1 x 10^{-4} g/g carbon fiber]
4. Adsorption time [min]

For production of composites with good fiber/matrix adhesion this contamination of the fiber surface with water must be greatly reduced by drying, e. g., by heating the carbon fiber before impregnation with thermoplastics.

3.4 Process concept for continuous fiber impregnation

The need for fiber drying in continuous impregnation of carbon fibers with polycarbonate and polysulfone from solutions was satisfied by a preliminary drying oven (Figure 6).

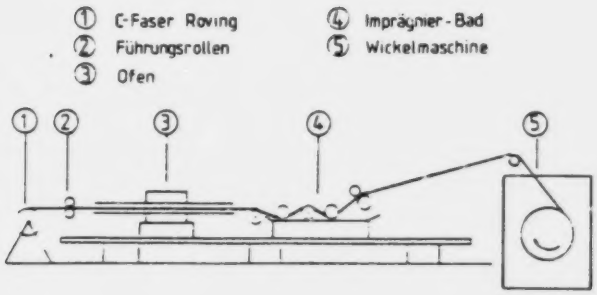

Figure 6. Schematic representation of a continuous carbon fiber impregnation plant for production of prepregs with thermoplastic matrices.

1. Carbon fiber roving
2. Guide rolls
3. Oven
4. Impregnating bath
5. Winding machine

Exact maintenance of the polymer solution composition and the fiber tension in wet winding are decisive for the quality of the composite. With insufficient fiber tension the strand forms a ring shape with a hollow core in the center (Figure 7, left half). Only with sufficiently high fiber tension does the impregnated carbon fiber bundle remain spread out in the flat shape desired (Figure 7, right half).

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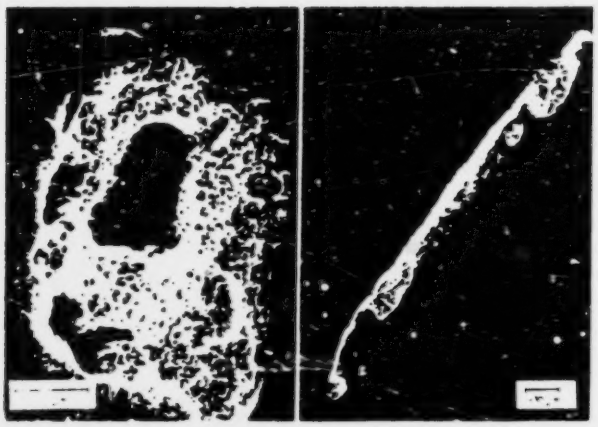

Figure 7. Carbon fibers in the prepreg with different fiber tension during impregnation: insufficient (left side); optimized (right side).

This thin tape form also allows drying of the fiber strands in the minimum time. If the fiber strand takes the shape of a tube it becomes difficult to transport all the solvent by diffusion from the inside of the tubular strand to the outside within the desired minimum drying time.

Figure 8 shows selected drying cycles for polycarbonate and polysulfone. A 12-hour drying at room temperature and normal pressure follows pre-drying at 12 Torr and 120°C as well as one drying cycle at 10^{-4} Torr and 150°C for polysulfone or 110-120°C for polycarbonate. This last step leads to complete removal of the solvent after 10 to 15 hours.

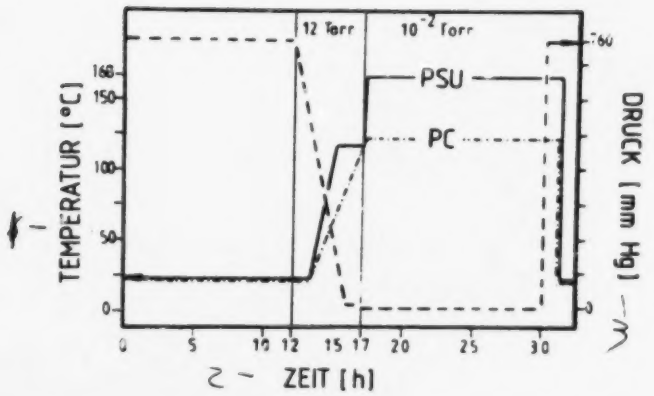

Figure 8. Drying cycles for prepregs with PC and PSU as the matrix.

1. Temperature [°C]
2. Time [hrs]
3. Pressure [mm Hg]

The nomogram shown in Figure 9 is intended to simplify the production of laminates with defined fiber volume contents. For a formed part with the carbon fiber Hercules AS 4 with dimensions of width = 1 m, length = 1 m and thickness = 2 mm, then, for example, the prepreg must have a weight of some 3100 g for a fiber content of 55% by volume with a 10% aexcess of polycarbonate. This kind of representatin can be established for any other fiber type and for any matrix.

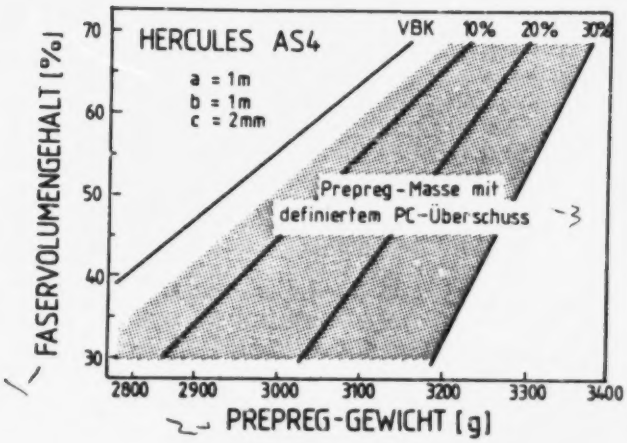

Figure 9. Nomogram to simplify production of laminates with definite established fiber volume content

1. Fiber volume content [%]
2. Prepreg weight [g]
3. Prepreg mass with definite PC excess

/ 5

4. Production of unidimensional composites from carbon-fiber-reinforced polycarbonate and polysulfone thermoplastics

Reproducible production of unidimensional samples is a prerequisite for systematic study of composite properties. The method of pressing laminates to make composite shapes was used in this work. It was found in preliminary experiments that the following points must be noted in the preliminary step of prepreg production:

1. Contamination of the carbon fiber surface by adsorption of moisture from the air is prevented by heating the fiber immediately before infiltration.
2. Adequate drying of the prepreg (removal of solvent) must assure that the glass temperature of the matrix is not displaced to excessively low values.

It is shown in the following that the viscosity of the matrix in the pressing process decisively affects the quality of the composite. It was found that determination of the flow behavior of matrix materials by means of the test temperature of TMA measurement (thermomechanical analysis) under inert gas can be used as a simple method.

The viscosity behavior of polycarbonate under stress as a function of the test temperature can be seen in Figure 10 (dashed line). A slight drop in viscosity occurs in the temperature region about 150°C, followed by a shoulder that drops off sharply above about 190°C and moves to a lower level of viscosity above about 200-230°C. From this, satisfactory flow behavior for working of polycarbonate laminates into composites at moderate pressure can be expected from polycarbonate above about 200-230°C.

For polysulfone (solid line in Figure 10) an expansion of the matrix occurs about 200°C. This is before reaching the region of low viscosity and good flow behavior. This anomaly must be taken into consideration in composite production. If the press pressures are very high with compression of prepregs in this temperature range, the added thermal expansion of the matrix will cause further strong compression of the composite and finally, fiber movement within the pressed shape. The compression

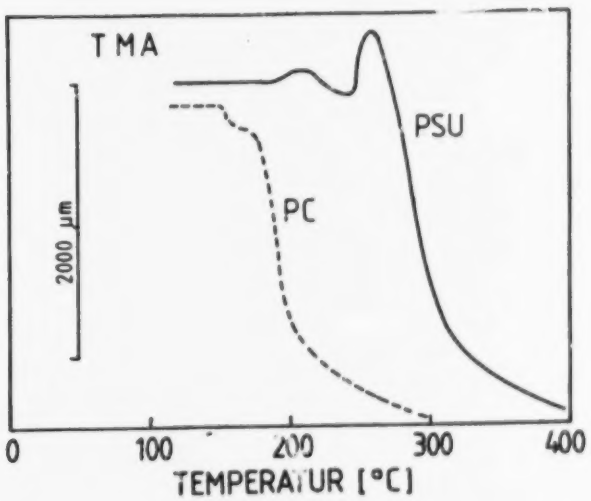

Figure 10. Viscosity behavior of PC/PSU, determined by thermomechanical analysis.

pressure for these materials, then, should be moderately increased only after exceeding 300°C. / 6

Without consideration of this special viscosity and expansion behavior within a narrowly limited temperature interval, severe thermal stresses would be produced in the composite, degrading the composite properties such as adhesion and bending strength. Therefore the temperature gradients within the pressed shape should be determined before the real pressing process.

Figure 11 shows the investigations done at constant compression temperature with the press shapes available. For polycarbonate processing temperatures about 240°C (dashed line) as well as for higher stressing temperatures, such as those for polysulfone, one can see a sharp temperature drop in both outer zones of the press mold. Therefore, both the outer 2 cm pieces were removed from the model composite before the measurement.

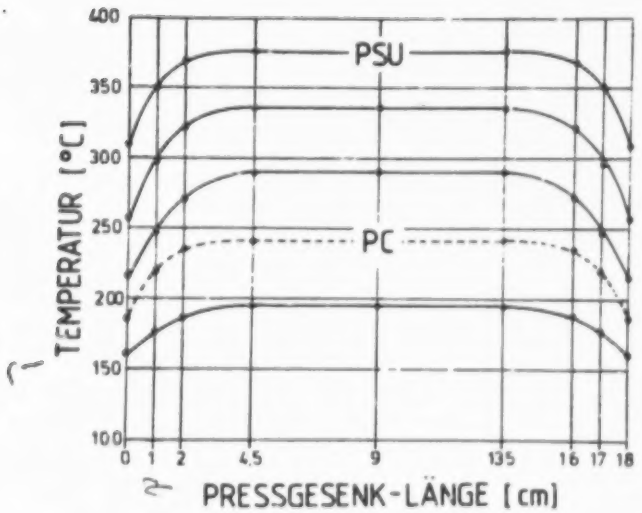

Figure 11. Temperature gradients within the press molds used for pressing the thermoplastic composites.

1. Temperature [°C]
2. Press mold length [cm]

Figures 12 and 13 show the attainable shear strengths in composites versus the applied press temperature and pressure for both polycarbonate and polysulfone with one of each of the fiber types. First, the optimal process temperature giving the best shear strength in the composite was determined at a constant compression pressure and a residence time of 20 minutes under the heated plate. The best composite properties were achieved, for instance, at pressing temperatures of 220-230°C for polycarbonate reinforcement and 350°C for polysulfone reinforcement. Then the press pressure was varied. The maximum interlaminar shear strengths were achieved above 190 bar

for polycarbonate or 220 bar for polysulfone. Higher compression pressures lead to no further improvement of the adhesion properties. The transverse photographs in Figure 14 show that the improvement in shear strength can be explained by improved fiber distribution in the composite.

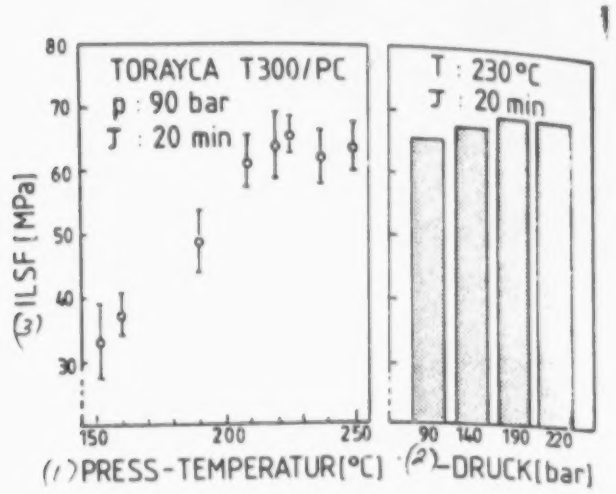

Figure 12. ILSS optimization in production of PC composites vs. temperature (left side) and press pressure variation (right side).

1. Press temperature [°C]
2. pressure [bar]
3. ILSS [MPa]

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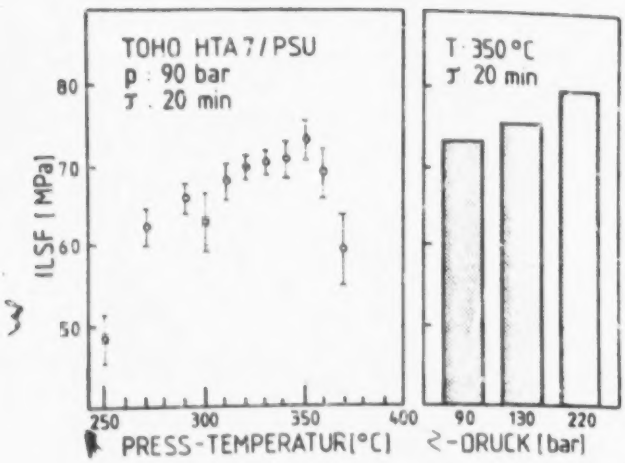

Figure 13. ILSS optimization in production of PSU composites vs. temperature (left side) and press pressure variation (right side).

1. Press temperature [°C]
2. pressure [bar]
3. ILSS [MPa]

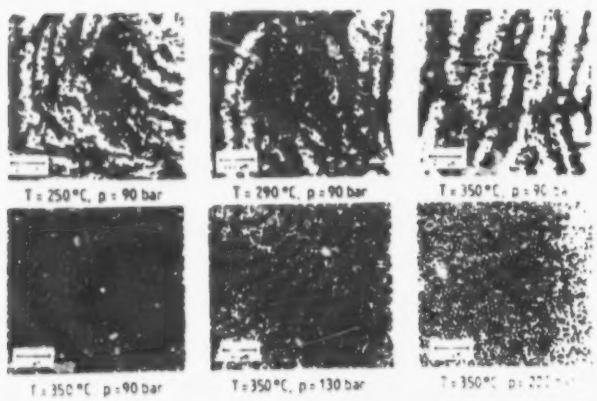

Figure 14. Fiber distributions in PSU composites with different press conditions.

5. Effect of fiber/matrix adhesion on utilization of the fiber strength in the thermoplastic composite

5.1 On utilization of the fiber strength in the composite

According to the mixing rule, it should be possible to predict the strength and E-modulus of the composite from the fiber and matrix components if the adhesion is adequate and the fiber /7 orientation is complete. These prerequisites are met only to a limited degree for the various technical methods of production. Figure 15 shows the bending strengths of composites of the same composition plotted as functions of the volume content of fiber.

One can see that the composite properties are quite different for different production methods. Therefore, one calculates the fiber utilization, or, better, the degree of transfer of fiber strength to the composite properties. This is calculated from the ratio of the actual composite strength to the theoretically predicted characteristic. This degree of utilization is shown on the right ordinate scale for a fiber volume content of 50%. For instance, with the pultrusion process (very highly parallel lay of fibers) one sees almost 100% fiber utilization. With the hand laying process one sees utilization only of the order of 60%, and 15% for the short fiber reinforcements. (If one actually had isotropic distribution of the short fibers, one would have to expect 1/6 of the fiber strength predicted by the mixing rule.) By means of stronger orientation, one gets anisotropic values, which are higher

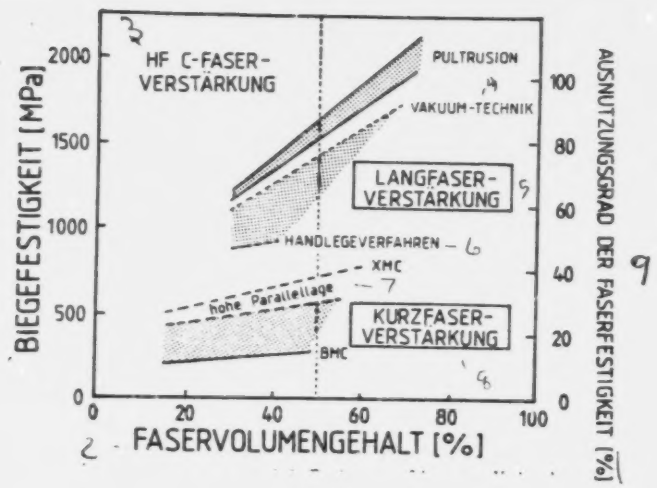

Figure 15. Bending strengths and fiber strength utilizations for composites attainable by various industrial production methods by means of varying the degree of filling with reinforcing fibers.

1. Bending strength [MPa]
2. Fiber content by volume [%]
3. High-strength Carbon fiber reinforcement
4. Vacuum technique
5. Long fiber reinforcement
6. Hand-laying process
7. highly parallel laying
8. Short fiber reinforcement
9. Degree of utilization of fiber strength [%]

in the short fiber direction than for the theoretically predicted isotropic distribution, but which are clearly below the prediction for exact parallel lay of the long fibers.

For the unidimensional model composites produced by optimized press compression processes, one can assume the prerequisite of exact parallel lay. The experimentally measured fiber utilization can, then, be directly correlated with the degree of adhesion between fiber and matrix.

5.2 Influence of adhesion

From previous experiments [36] on reinforcement with reactive matrix systems such as epoxides and polyimides it was well known that adequate adhesion between fibers and matrix is possible only if both the matrix and the fiber have a sufficient proportion of reactive centers which can interact with each other.

Given the reactivity of the matrix to be reinforced (polycarbonate or polysulfone), variation of adhesion is possible only through altering the surface properties of the carbon reinforcing fibers. Reactive centers on the fiber surface are superficial oxides of acidic or even basic nature, formed through oxidation of the carbon fiber surface (Figure 16).

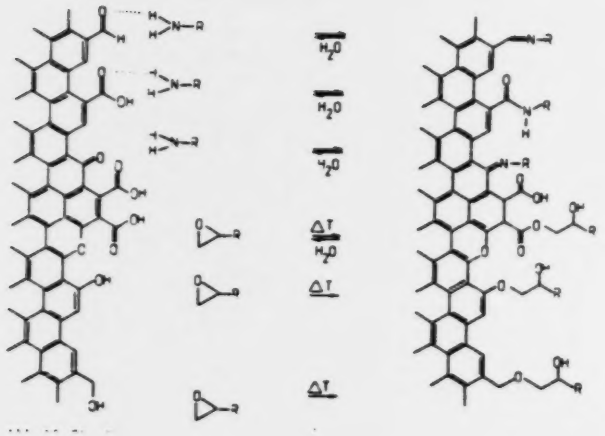

Figure 16. Surface groups on high-modulus carbon fibers and possible reactions with the functional groups of epoxy resin / amine hardener mixtures.

Table 2 summarizes the three important methods for oxidative surface treatment of carbon fibers [37].

Table 2. METHODS OF OXIDATIVE SURFACE TREATMENT OF CARBON FIBERS

Method	Wet oxidation	"Dry" oxidation	Anodic oxidation
Medium	HNO_3	Air, O_2, CO_2 Cl_2 and mixtures	H_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, NaOH
Temperature	90-110°C	400-900°C	20-40°C
Residence	0.5 - 10 hr	0.5 min - 2 hr	0.5 - 10 min

Three important methods of oxidative surface treatment of carbon fibers are summarized in tabular form in Table 3 [37].

In principle, this oxidation can be done by wet chemistry, e. g., in boiling sulfuric or nitric acid [38,39], thermally with or without catalysts (e. g., in air at temperatures above 400 °C [40,41]), or by anodic oxidation in aqueous electrolytes [42-44].

Nearly all surface oxidation processes, though, not only produce surface groups but also cause change of the surface topography, which is expressed in a change in the BET surface area [45].

Slow wet oxidation of high-modulus carbon fibers was investigated for the systematic variation of surface treatment described here so that the results could be compared with previous systematic studies.

As Figure 17 shows, the initial adhesion for both polycarbonates and polysulfones rises from 30 MPa to about 50 MPa after some 72 hours of oxidation of the carbon fibers in boiling concentrated nitric acid. The ILSS value of the reinforced polysulfone is slightly above that for reinforced polycarbonate with the same fiber type. Bending strengths of both reinforced matrix systems (same reinforcing fiber) give a bending strength about 920 MPa after 72 hours of oxidative surface treatment. In all the studies of bending strength the breaking elongation of the composite is between 0.55% and / 9 0.63%, in the range of fiber elongation. Thus, for

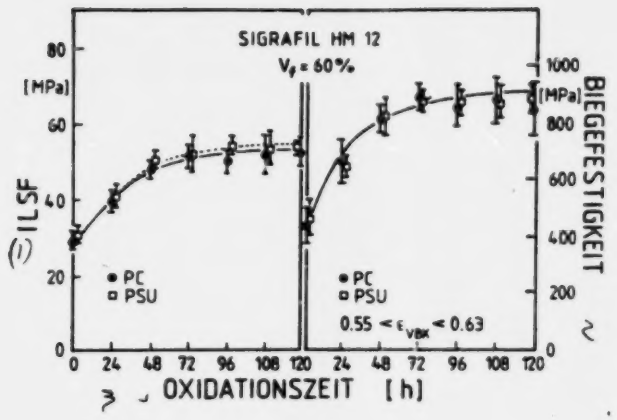

Figure 17. ILSS (left side) and bending strengths (right side) of composites with reinforcing fibers with wet chemical activation (boiling 68% HNO_3) for various times.

1. ILSS (interlaminar shear strength)
2. Bending strength3. 3. Oxidation time [hr]

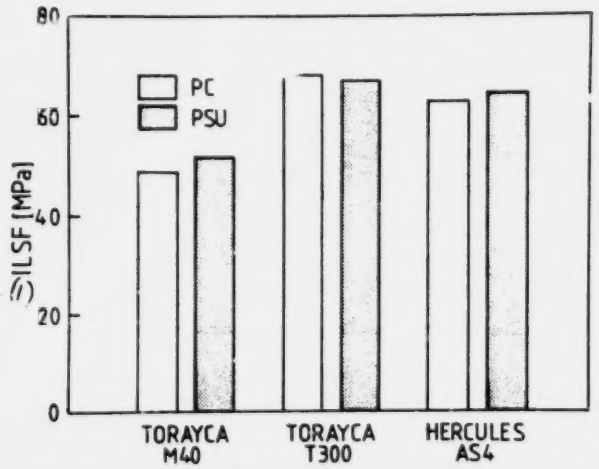

Figure 18. ILSS values attainable on reinforcement of PC/PSU with commercial carbon fibers.

1. ILSS

reinforcement of polycarbonate and polysulfone with high-modulus carbon fibers, the fiber elongation appears to be the limiting component.

Figure 18 shows ILSS values for components with industrial surface-treated high-modulus as well as high-strength carbon fibers.

Reinforcement with TORAYCA M40, a high-modulus type, gives an upper ILSS value of some 50 MPa. Reinforcement with high-strength fibers (TORAYCA T 300 AND HERCULES AS 4) gives higher adhesion values, as previously observed for reinforcement of epoxy resin systems. This could be due to the higher reactivity of the surface of this type of fiber. Newer studies show that for this fiber type both the oxygen-containing groups generated by surface oxidation and the nitrogen components contained in the precursors of the fibers contribute to adhesion [46].

Comparison of the bending strenghts of these two fiber types as reinforcing fibers in the thermoplastic systems (Figure 19) shows that strengths of about 800-900 MPa are achieved with the high-modulus type (HM 125, M40-40B). Poorer utilization of the fibers due to inadequate surface activation yields strengths of about 400 MPa (Fiber HM 12 U). Higher bending strengths can be attained with high-strength fiber reinforcement. Reinforcement with the high-strength fibers TORAYCA T 300, TOHO HTA 7 and HERCULES AS 4 shows further that the fibers with best adhesion in both matrix systems do not exhibit the highest bending strength. This is due to the substantial contribution of the fiber strength to the bending strength of the composite.

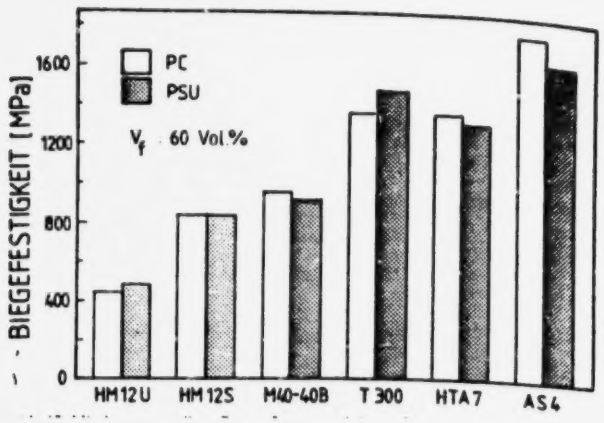

Figure 19. Bending strengths attainable in PC/PSU reinforcement with commercial carbon fibers.

1. Bending strength [MPa]

5.3 Limitation of fiber utilization by the fiber volume content in the composite

The significance of the strength behavior for reinforcement of thermoplastic systems is clarified through the investigation of the dependence of bending strength on the fiber volume content. The HERCULES AS 4 fiber type was used in this study because it was the one with maximum bending strength in the investigations at 60% fiber content by volume (Figure 20).

By comparison with reinforcement of reactive epoxy resin systems, a linear increase in bending strength would be expected with rising fiber volume content, in accordance with the mixing rule. This mixing rule is confirmed for polycarbonate and

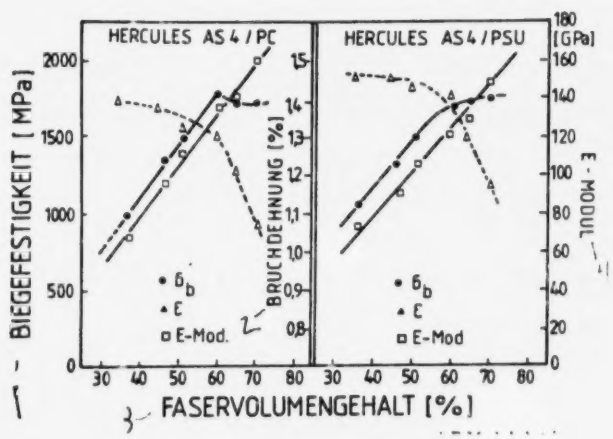

Figure 20. Change of bending strength, breaking elongation and E modulus with the volume content of the reinforcing fiber HERCULES AS 4 in PC (left side) and PSU (right side).

1. Bending strength [MPa]
2. fracture strain
3. Fiber volume content [%]
4. E-modulus

polysulfone reinforcement up to the fiber volume range about 60% by volume. In a thermoplastic system, exceeding this critical limiting concentration of fibers leads to further rise in the E modulus according to the mixing rule. But the simultaneous drop in the composite elongation leads to a nearly constant strength value. This behavior is observed for both matrix systems and needs explanation.

6. Breaking behavior /10

The following explanation is offered for the result of the limitation of fiber utilization at a fiber content of 60% by volume (preceding section) (accurate analysis of the breaking behavior of this reinforced thermoplastic):

Crushing of the composite in the compression region of the stress zone leads to crack initiation, starting from this stressed location and going across into and through the composite (Figure 21) [60].

This observation is completely contradictory to strength studies with brittle carbon-fiber-reinforced reactive resin systems. There, damage analysis shows essentially a failure in the tension region of the composite. This is shown in Figure 22.

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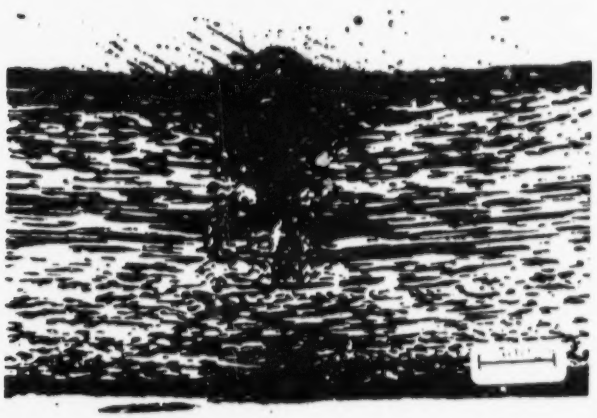

Figure 21. Cross-section of a unidimensional PSU composite slightly damaged in the compression region by bending load.

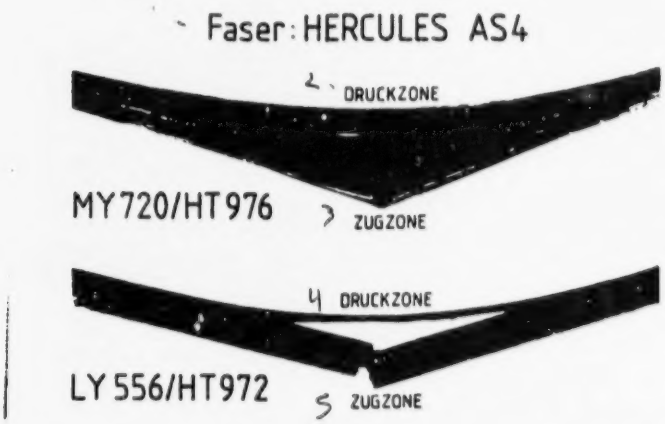

Figure 22. Epoxy resin composite failing in the tension region on bending stress.

1. Fiber: HERCULES AS 4
2. Compression zone
3. Tension zone
4. Compression zone
5. Tension zone

7. Effect of avivage and its function as an intermediate layer in the composite

Commercially available fibers have a fiber finish intended primarily to allow better manipulation of the fibers. On the other hand, there is the potential for using this "finish" as an adhesion improver between the fiber and the matrix. Because of the extremely high processing temperatures for the thermoplastics being studied here, the thermostability of this finish to be applied by the producing company to the fiber surface is of the highest importance.

If the thermal decomposition of a commercially applied finish occurs before reaching the actual processing temperature for pressing into a composite, there will be damage to the fiber/matrix interface, resulting in lower adhesive and bending strength. Unfortunately, most of the various manufacturers provide no information about the finish compositions, which are classified as industrial "know-how".

As a result, the processor must test the thermal compatibility of the fiber finish before processing. As an example, Figure 23 shows the weight loss of three selected commercially available carbon fiber types with rising temperature under inert gas. No marked mass loss on thermal heating is measured up to the press temperature range for polycarbonate reinforcement (press temperature about 230°C). Therefore, these three fiber types with their industrial finish can be used for polycarbonate reinforcement if there is no chemical incompatibility. Above 250°C, though, these three fiber types studied diverge decisively from each other: For the fiber HERCULES AS 4 W 12 the mass loss up to 350°C is only about 0.2% by weight, while

the loss for TORAYA T 300 is about 0.4%, and for TOHO HTA 7 it is even 0.6%. Of these three fiber types studied, then, only the fiber HERCULES AS 4 W 12 can be used as is for polysulfone reinforcement. In order for the other two fiber types to be made useful for polysulfone reinforcement they would first have to be subjected to several days of extraction. That would completely remove the corresponding "industrial finish".

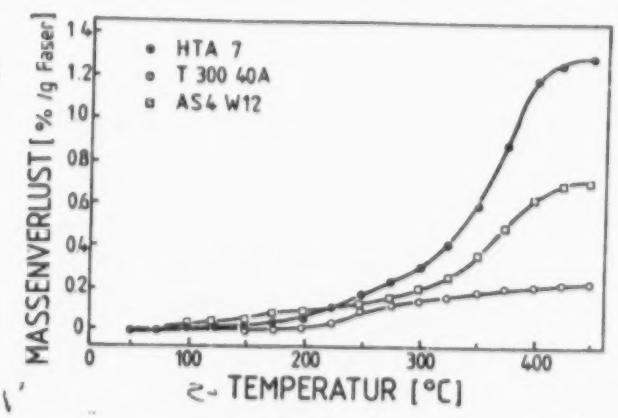

Figure 23. Testing the thermal behavior of commercially finished carbon fibers by thermogravimetry.

1. Mass loss [%/g fiber]
2. Temperature [°C]

In the following, suitable finish compositions for thermoplastic reinforcements are discussed:

i) our own finish
ii) foreign finish

Because of the intermediate layers used, the interlaminar shear strength (ILSS) increases both for polycarbonate reinforcement and for polysulfone reinforcement (Figure 24). Bare HERCULES AS 4 fiber was used as the reinforcing fiber. The improvement in adhesion, going from the unfinished fiber through commercial fiber finish to our own finish P1700 can be brought into agreement with the moisture uptake of the fiber (Figure 5). The possible accumulation of water at the reactive centers of the fiber surface leads to reduction of the activity between the fiber and the thermoplastic matrix.

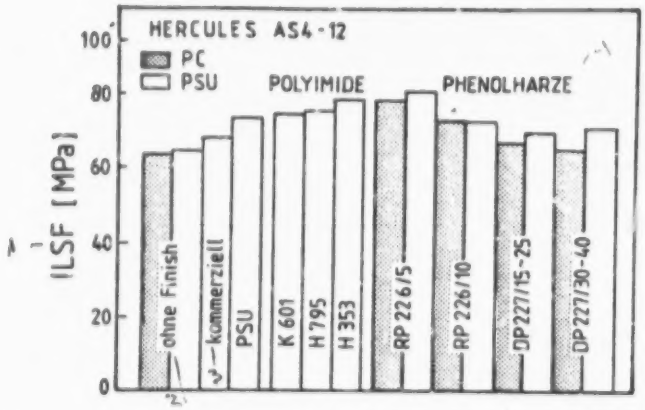

Figure 24. Effects of different finish systems on the ILSS of the carbon-fiber-reinforced thermoplastics PC and PSU.

1. ILSS [MPa]
2. unfinished
3. commercial
4. phenolic resin

The selected finish reduces this water adsorption /11
-- the adhesion rises. An increase in ILSS is also observed by aplication of hard polyimide finish (K601, H795, H353). The exact cause for this further improvement in adhesion is not known, but could be due to the decreased water uptake of this polyimide. With use of phenolic resins, the phenolic resin provides the greatest adhesion with the lowest cross-link density.

The results of bending strength studies with intermediate layers as finishes are shown in Table 3. All intermediate layers lead to higher beinding strengths than for reinforcement of the particular thermoplastic matrix with the unfinished starting fiber HERCULES AS 4. The strength values for reinforcement with polycarbonate are higher by 100 - 200 MPa than for those with a polysulfone matrix.

Because of the hardness of the phenolic resin finish used (maximum bending strengths are obtained), crack propagation can occur inside the brittle intermediate layer under stress. The load limit of the fiber is, therefore, reached only with considerably higher applied stresses. The breaking load of the composite is increased, and this can be observed in most of the experiments done with intermediate layers.

Table 3. EFFECT OF DIFFERENT FINISH SYSTEMS ON BENDING STRENGTH PROPERTIES OF THE REINFORCED THERMOPLASTICS PC AND PSU

	Finish	Bending strength MPa	Breaking elongation %	E-modulus GPa
PC	-	1772	1.30	136
Phenolic resin	RP 226/5	1867	1.44	130
	RP 226/10	1726	1.36	127
	DP 227/15-25	1964	1.60	123
	DP 227/30-40	1987	1.49	133
PSU	-	1617	1.40	116
Polyimide	K 601	1518	1.34	114
	H 795	1740	1.38	126
Phenolic resin	RP 226/5	1765	1.39	127
	RP 226/10	1710	1.37	125

Technologically, thermal treatments are used to increase the resistance of the composite to thermal deformation [47]. On areinforcement of the polysulfone thermoplastic (P 1700), not only is the thermal deformation resistance increased on reinforcement, but simultaneously also the ILSS of the composite is increased (Figure 25). This improvement in adhesion, along

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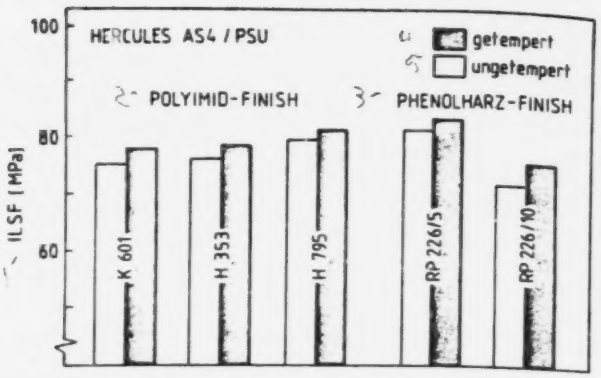

Figure 25. Increase in ILSS due to thermal treatment of finished composites.

1. ILSS [MPa]
2. Polyimide finish
3. Phenolic resin finish
4. annealed
5. not annealed

with the increase in strength of the matrix, also indicate an increase in the fiber/matrix reactivity.

8. The behavior of carbon-fiber-reinforced thermoplastics at cryogenic and slightly elevated temperatures

The extremely high breaking elongations of polycarbonate and polysulfone (60% and 50% respectively, see Figure 2) suggest that these matrix materials are suitable for low-temperature technology (use down to temperatures about 4.2 °C) [29,48]. Commercial matrix systems such as semiflexible and ductile epoxy resins show breaking elongations about 1.5 - 2% in this temperature range [30, 49, 50]. These are about the breaking elongations of the fibers, so that at these temperatures there are brittle fractures of the composites under stress. The breaking elongations of polycarbonate and polysulfone at 77 K are about 9% and 7%, respectively, and are still above 3% at 4.2 K [51]. Therefore, use of these matrix materials should be able to prevent brittle fracture.

Figure 26 shows a comparison of the fracture behavior of semiflexible epoxy resin LY 556 with that of the two thermoplastics, polysulfone and polycarbonate, each reinforced with the fiber HERCULES AS 4 (test temperature 77 K). Delamination under load can be detected for the epoxy resin composite.

Fracture of the composite occurs at an elongation near 2%. The matrix systems polysulfone and polycarbonate, in comparison, show flow behavior with constant load distribution, even past 2% elongation for the composite. Further reduction of temperature down to 4.2 K leads to a smooth brittle fracture of the epoxy resin composite, while the flow process remains unchanged for the polysulfone and polycarbonate. This surprising behavior is

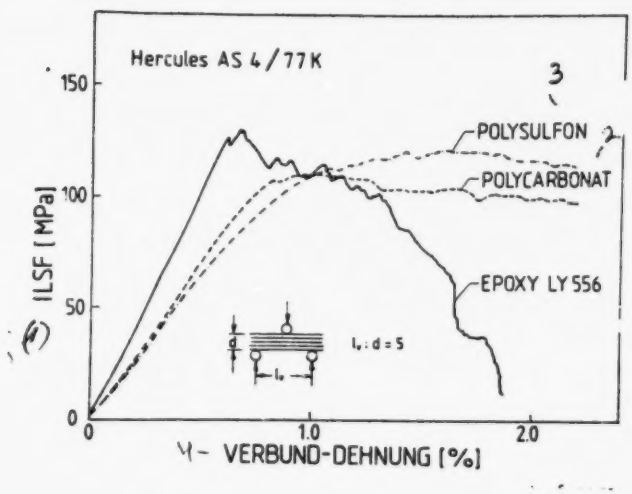

Figure 26. Comparative examination of failure of composites of carbon-fiber-reinforced epoxy resin LY 556, PC and PSU.

1. ILSS [MPa]
2. Polycarbonate
3. Polysulfone
4. Composite elongation [%]

not yet explainable. We checked for the occurrence of 'crazes' within the matrix, as 'craze opening' might then have been responsible for this abnormal elongation behavior.

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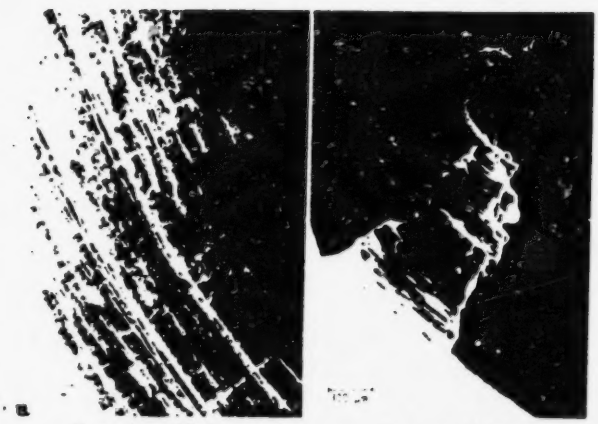

Figure 27. SEM picture of the site of failure with a short-bend load (ILSS measurement) of composites at 77 K: permanent deformation (left side: high-strength carbon fiber) and tensile failure with fiber pull-out (right side: high-modulus carbon fiber).

Figure 27 shows scanning electron micrographs of composites with a polycarbonate matrix. The left half of the picture shows the permanent deformation after stress with reinforcement with the high-strength carbon fiber HERCULES AS 4. The right half of the picture shows the fracture propagation and the surprisingly /12 observed 'fiber pull-out' on reinforcement with the high-modulus carbon fiber TORAYCA M 40 in spite of good adhesion behavior. The decrease in matrix elongation to only 9% at this temperature prevents both a smooth brittle fracture such as is observed for high-modulus carbon-fiber-reinforced epoxy resins, and also compression failure of the composite. The limiting magnitude for this 'bending test' appears to be the tensile strength of the fiber. In no case, though, may we speak of an interlaminar shear strength measurement (there the failure action would have

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to occur in the neutral zone, i. e., in the middle of the composite). Rather, we can speak of a short bend fracture. The force measured over this short bending fracture, therefore, does not directly reflect the adhesion between the fiber and the matrix surface.

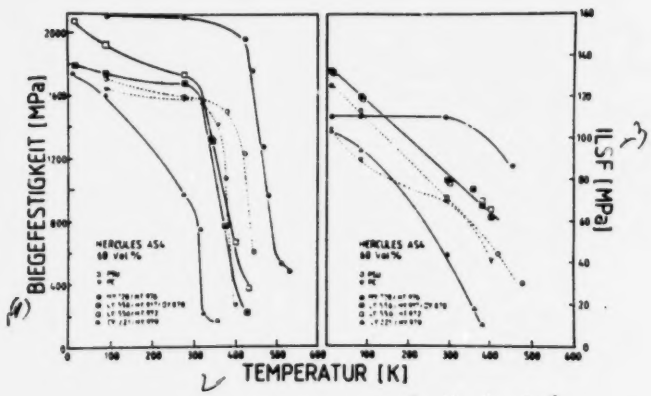

Figure 28. Comparison of strength of carbon-fiber-reinforced epoxy with carbon-fiber-reinforced PC/PSU in the temperature range 4.2 K to 600 K.

1. Bending strength [MPa]
2. Temperature [K]
3. ILSS [MPa]

Figure 28 contains a comparison of the bending strengths of four epoxy resin systems (solid curves) with the thermoplastics, polycarbonate and polysulfone (dotted curves). The comparison shows that in thermal strength behavior, only the tetrafunctional MY 720 system shows high thermal strength properties like polysulfone and polycarbonate (left half of the figure). The range of use for carbon-fiber-reinforced

polycarbonate extends up to 120 °C, and that for carbon-fiber-reinforced polysulfone up to 160 °C. With the epoxy resins as matrix, the attainable bending strengths are higher at room temperature and below. This is due to the effect of the matrix strength on the bending strength.

The adhesion behavior, shown by the measurement of the ILSS in the right half of the figure, is also distinct from that of the epoxy resins. Both thermoplastics show lower ILSS values at room temperature than those of the two semiflexible LY 556 systems and the brittle MY 720 system. Only the semiflexible CY 221 system at 40 MPa is some 30 MPa below the value for reinforces polycarbonate/polysulfone. With decreasing temperature the ILSS rises steeply in all the systems studied (except for MY 720), up to values of about 130 MPa for polysulfone and LY 556 [52, 53]. The increase in ILSS with decreasing temperature can be ascribed to two effects:

i) increase in matrix strength [54]

ii) shrinkage of the matrix onto the fiber [29].

The latter effect of shrinkage is specially discussed in [52].

9. Impact resistance behavior of carbon-fiber-reinforced thermoplastics.

It is well known that behavior under impact stress is a severely limiting factor for the modern high-strength composites. The use of thermoplastics with far higher breaking elongations than the commercial matrix systems such as epoxides and polyimides should, therefore, lead to a significant reduction of impact sensitivity for carbon-fiber-reinforcement.

A comparison of the impact resistance of the previously discussed epoxy resins with those of polycarbonates and polysulfones is plotted in Figure 29 as a function of the matrix elongation [55]. The work of breakage was determined with a Charpy pendulum machine.

The impact resistance of epoxies increases nearly linearly with increasing elongation of the pure resin. The thermplastics, polycarbonate and polysulfone, with impact resistances of about 60 KJ/m² for polysulfone and 140 KJ/m² for polycarbonate, depart from this linearity. A dependence of the impact resistances of the pure matrix systems on their elongation can be detected.

/13

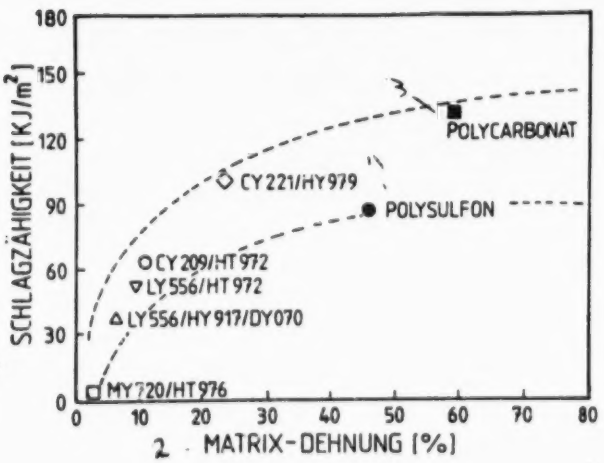

Figure 29. Impact resistances of the pure matrix systems, plotted vs. their elongations.

1. Impact resistance [KJ/m²]
2. Matrix elongation [%]
3. Polycarbonate
4. Polysulfone

Figure 30 shows these results transferred to carbon-fiber-reinforced composites. The impact resistances for the pure matrices are shown cross-hatched, and those of the composites with the reinforcing fiber HERCULES AS 4 are shown as open columns. For all the reactive matrix systems, reinforcement with the fiber type HERCULES AS 4 (fiber volume content 60%) yields the same impact resistance, both for the case of the thermoplastic systems (polycarbonate and polysulfone) as well as for each variation of hardness of the epoxy resins (hard tetrafunctional MY 720 up to the semi-flexible CY 209) [56].

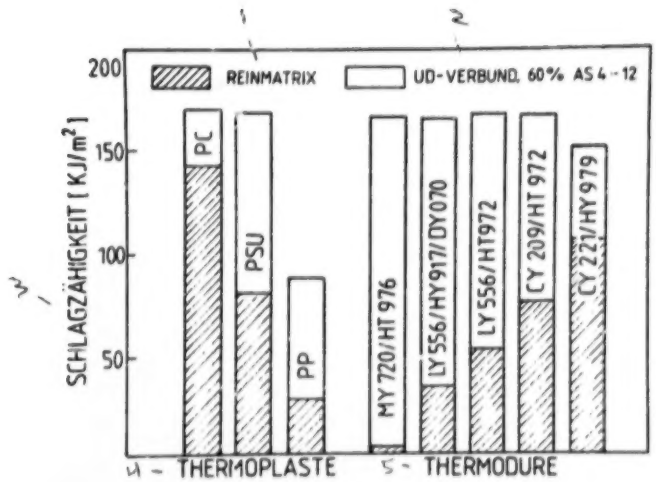

Figure 30. Impact resistances of the pure matrix systems (thermoplastics and thermosets, hatched columns) compared with their unidimensionally carbon-fiber-reinforced composites (open columns).

1. Pure matrix
2. Unidimensional composite, 60% AS 4-12
3. Impact resistance [KJ/m²]
4. Thermoplastics
5. Thermosets

For composites with these high fiber volume contents, the elongation of the matrix shows little, or only minimal, effect on the impact resistance. Figure 31 shows the testing of these results for different fiber volume contents, and for reinforcement both with high-strength and high-modulus fibers [55].

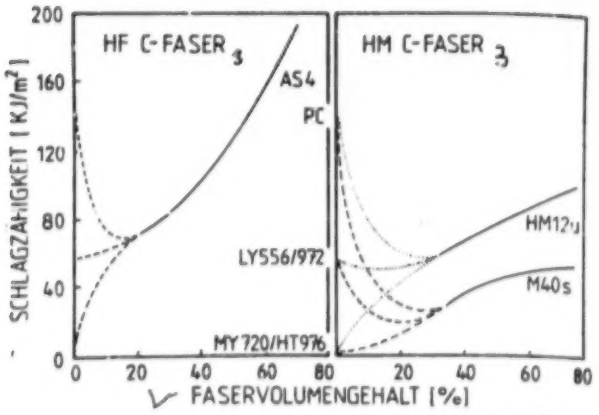

Figure 31. Impact resistance behavior of composites with different proportions of carbon fibers in thermosetting and thermoplastic matrices on reinforcement with surface-activated (AS 4, M 40 S) and non-activated (HM 12 U) carbon fibers.

1. Impact resistance [KJ/m²] 3-fiber
2. Fiber volume content [%]

The effect of the matrix on the impact resistance is visible at fiber volume contents below 20-30% by volume for high-strength fiber reinforcement and below 40% by volume for high-modulus carbon fibers. Reinforcement of matrix systems with hard carbon fibers does not, however, lead in every case to reduced impact resistance. Rather, depending on the impact resistance of the matrix, the fibers can, even from the beginning, give an improvement in impact behavior of the composite (compare the reinforcements with epoxy resins LY 556 and MY 720). Above 50%

by volume for the case of high-strength reinforcement of polycarbonate even the high initial impact resistance of the pure matrix is exceeded. This is not possible with reinforcement by high-modulus carbon fibers.

The additional effect of surface treatment of the carbon fibers (s: surface-treated; u: untreated) on the impact resistance is clarified for the high-modulus carbon-fiber-reinforcement. HIgh-modulus fibers which are not surface-treated, when used as reinforcing fibers in polymer matrix systems yield higher impact resistances than fibers that are surface-treated [57].

10. Effect of humidity on adhesion and impact resistance

For carbon-fiber-reinforced epoxies, it is well known that after holding in boiling water the strength can drop to 50% of the initial strength. There is still no clear explanation of whether this is due to damage to the matrix or to the fiber/matrix boundary. Damage to the fiber itself can be ruled out.

It was known that carbon-fiber-reinforced thermoplastics also suffer loss of strength on holding in water, but to a lesser extent. Even with water attack under more severe conditions, the thermoplastic composite is considered superior to the epoxide composite.

Our own experiments on water exposure for the model composites discussed here gave decreases in strength of some 5 - 10% after 250 hours exposure at room temperature, and about a 20% drop in strength at 100°C (see Table 4).

Table 4. REDUCED BENDING STRENGTHS OF REINFORCED PLASTICS PC AND PSU AFTER 250 HOURS IN COLD AND BOILING WATER

MATRIX	BENDING STRENGTH (MPa)		
	Time in Water		
	None	250 hrs/ 25°C	250 hrs/ 100 °C
PC	1771	1574	1426
PSU	1617	1503	1389

Now it was necessary to clarify whether this drop is due to a boundary effect or to a matrix effect.

Figure 32 shows that adhesion in a composite after 250 hours storage in water decreases below the value for adhesion of the composite when reinforced with the untreated high-strength initial fiber. Quite certainly, the water attacks the surface oxides generated by the surface treatment. In addition, the basic adhesion is even reduced below the value for the untreated starting fiber (see in this respect the effect of the nitrogen of high-strength carbon fibers on the chemical bonding [58]). /14

Both with room-temperature storage and with storage in boiling water, the composites greatly exceed the equilibrium water uptake for the pure polymers, polycarbonate and polysulfone (Figure 33, left half of figure).

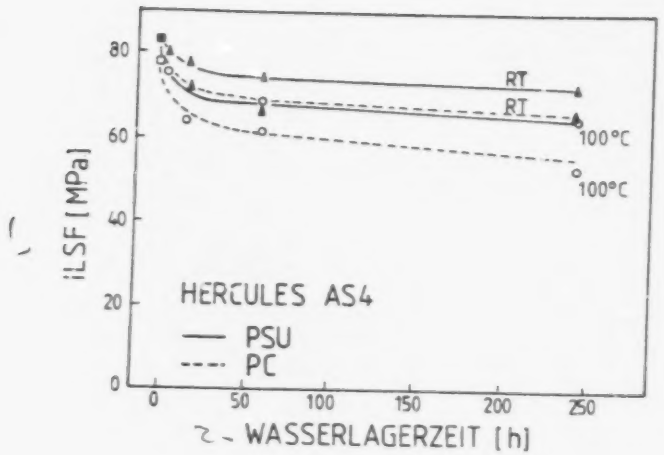

Figure 32. Decreasing ILSS of the PU/PSU composite with increased holding time in cold and boiling water.

1. ILSS [MPa]
2. Time in water [hrs]

Through introduction of reinforcing fibers, additional boundary surfaces between fibers and matrix are provided. The excess water uptake in the composite can, therefore, take place only at the fiber/matrix boundary. This agrees with the previous statement about the weakening of bonding detected through reduced ILSS values.

The right half of Figure 33 shows the effect of a drying treatment (air, 120°C).

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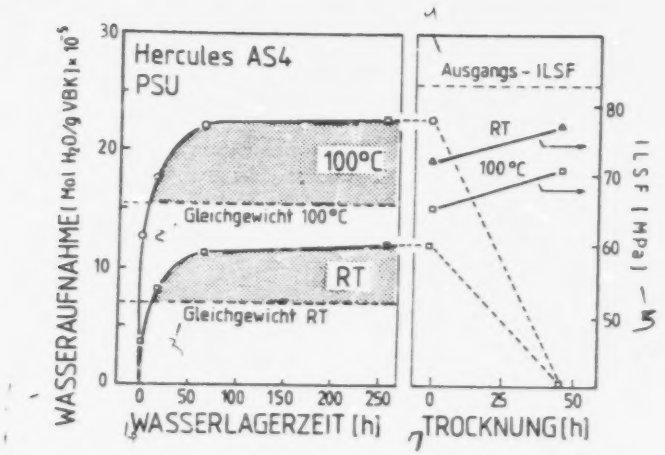

Figure 33. Water uptake of composites beyond the maximum possible equilibrium water uptake for the pure PSU on holding in cold and boiling water (left side), and remaining damage to the ILSS due to irreversibly absorbed water (right side).

1. Water uptake
2. Equilibrium, 100°C
3. Equilibrium, RT
4. Initial ILSS
5. ILSS [MPa]
6. Time in water [hrs]
7. Drying [hrs]

Drying of the composite after hydrolytic action leads to a total loss of the absorbed water, and the ILSS increases. However, it does not reach the initial value, as would be expected for the case of reversible water absorption. Therefore, the water attacks polar centers of the fiber surface and inactivates them irreversibly.

The damage to the fiber/matrix boundary activation due to water uptake can also be shown by means of impact resistance studies.

Figure 34 shows the decrease in impact resistance for the carbon-fiber-reinforced thermoplastics used here, and the drop in imipact resistance of the pure, unreinforced matrix material in the case of polycarbonate, while the polysulfone shows no change in impact resistance with increasing hydrolytic treatment. From this alone one can conclude that the drop in composite resistance in the case of the polysulfone must be ascribed solely to the damage to the boundary. In the case of the polycarbonate, damage to the matrix itself can play a part.

In Figure 30, p. 38-12, though, it is shown that for this arrangement for the impact resistance test (60% fiber content by volume, unidimensionally oriented) the effect of the matrix does not appear. Therefore, no added effect of the matrix in polycarbonate reinforcement can be seen in these experiments. It can be concluded, then, that reduction of the impact resistance of the composites is determined solely by the fiber/matrix boundaries.

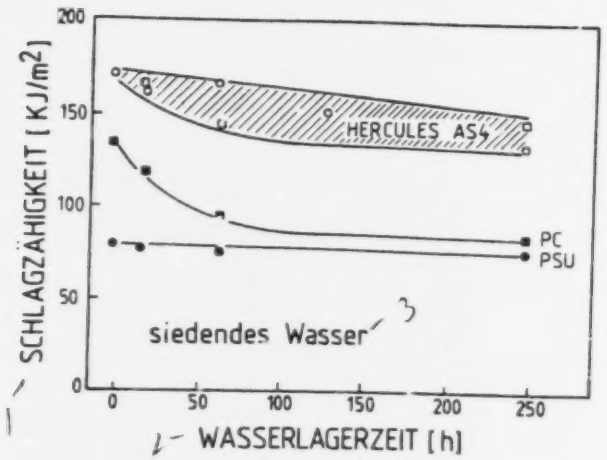

Figure 34. Effect of boiling water on the impact resistance of the pure thermoplastic PC/PSU (solid lines) and of carbon-fiber-reinforced PC/PSU (shaded area).

1. Impact resistance [KJ/m²]
2. Time in water [hrs]
3. boiling water

The excess water taken up by the composite (some 40 x 10^{-6} moles per gram of fiber) is sufficient for full blocking of the active surface centers generated by the industrial surface treatment process. (The amount of surface oxides detectable by desorption studies and by titration is some 20 x 10^{-6} moles per gram of fiber.) This also explains the impact resistance /15 behavior of composites after storage for more than 1,000 hours

in boiling water: the impact resistance does not decrease significantly below that for reinforcement with untreated fibers.

11. Conclusions

1. It could be shown that the relatively high-melting thermoplastics, polycarbonate and polysulfone, can be processed in solution to yield pore-free laminates. In spite of homogeneous fiber distribution, the fiber utilization is only about 70%. This limitation of the fiber utilization by the volume proportion of fibers can be explained through compression failure of the composite.

2. The importance of the oxidative surface treatment of the carbon fibers has been demonstrated. The improvement of shear strength by a factor of 2 to 3, similar to the case for reinforcement of epoxies, is explained through chemical interaction.

3. The finish of carbon fibers, to the extent that it is not declared by the manufacturer, must be tested by the user for its thermal stability. Otherwise it is impossible to reinforce successfully by hot pressing.

4. The finish can be used to improve adhesion by suitable selection of appropriate or compatible polymer systems. By means of suitable polymeric intermediate layers, the breaking mechanism [can be affected] so that the bending strength is increased. Polyimides, for instance, prove to be good as such intermediate layers for embedding in polysulfone and polycarbonate.

5. The adhesion and breaking strength of carbon-fiber-reinforced thermoplastics increases on reduction of the test temperature. Such composites may prove good for use at cryogenic temperatures.

6. The effect of increased temperatures causes weakening of the mechanical properties, as for thermosets, especially if the glass temperature of the matrix is exceeded.

7. Similar to the case for cross-linked thermosetting polymer matrices, testing of the impact resistance (pendulum blow on samples with 60% by volume) shows no effect of the thermoplastic matrix on the impact behavior. The limiting feature for impact resistance for composites above 40% by volume is, then, fiber elongation. Only at low fiber contents (below 30%) do the reinforced thermoplastics behave clearly better than the classical carbon-fiber-reinforced epoxies.

8. The water uptake for the reinforced thermoplastics is less than for the epoxies. The strength, correspondingly, decreases less than for the classical carbon-fiber-reinforced epoxies. (Rather extreme water uptake here: up to 20% for 100°C, 250 hrs).

It could be shown that this drop in strength is due almost solely to damage to the fiber/matrix interface. The improvement of adhesion due to surface treatment is almost completely eliminated. Even part of the basic adhesion is reduced.

To the extent that general conclusions can be drawn from the limited experimental preparation for the test work, it appears that carbon-fiber-reinforced thermoplastics are clearly

superior to the thermosets with respect to production and shaping. They are slightly inferior with respect to fiber utilization and definitely superior with respect to impact resistance. They are partially superior with respect to water uptake, but the basic problem of water damage and impact sensitivity of carbon-fiber-reinforced has not been solved.

LITERATURE

[1] G.W. Ehrenstein, Kunststoffe 60, 12 (1970)
[2] J. Englehardt, 22nd Annual Conference, Reinforced Plastics Division, SPI, 1967, Section 10-E
[3] R. Richards, D. Sims, Composites 2, 12 (1971)
[4] A. Bernardo, SPE J. 26 (1970)
[5] L. Goettler, Monsanto Research Corporation, HPC 72-149, December (1972)
[6] P. Petit, M.E. Waddoups, J. Composite Materials 3, 1 (1969)
[7] P. Mallick, L. Broutman, 29th Annual Conference, Reinforced Plastics/Composites Institute, SPI, 1974, Section 13-B
[8] L.J. Broutman, R.H. Krock, Modern Composite Materials, Reading, Mass. (1967)
[9] W.H. Sutton, J. Chorne, Fibre Composite Materials, Ohio (1965)
[10] A. v. Harnier, Kunststoffe 65, 2 (1975)
[11] M. Buhl, U. Neumann, Plastverarbeiter 31, 9 (1980)
[12] R.M. Ogorkiewicz, S. Turner, Conference on Reinforced Thermoplastics, Solihull, England, Plastics Institute (1970)
[13] S. Turner, R.M. Ogorkiewicz, 7th Int. Reinforced Plastics Conference, Brighton, England (1970), British Plastics Federation
[14] Y.L. Fan, 25th Annual Technical Conference, SPI (1970), Section 16-B
[15] J.B. Thomson, DOS 1948 138 (1970), US P 3585103 (15. 6. 1971)
[16] E.P. Plueddemann, Applied Polymer Symposium Bd. 19 (1972)
[17] E.P. Plueddemann, SPI 27th Annual Technical Conference (1972), Section 11-B, 21-B
[18] E.P. Plueddemann, Polymer Plan. Technol. Engng. Bd. 2 (1973), H. 1
[19] G. Lubin, ISBN 0-442-24897-0, Van Nostrand Reinhold Company Inc., N.-York
[20] E.P. Plueddemann, G. Stark, 32nd Annual Conference, Reinforced Plastics/Composites Institute, SPI, 1977, Section 4-C
[21] E.P. Plueddemann, G. Stark, 28th Annual Conference, Reinforced Plastics/Composites Institute, SPI, 1973, Section 21-E
[22] B. Blumentritt, B. Vu, S. Cooper, Composites 6, May (1975)
[23] Fiberfil Division, Dart Industries, Inc., Catalog No. 475-7854
[24] G. Hannes, Diplom-Arbeit, University of Karlsruhe, Institute for Chemical Technology (1983)
[25] W. Hüttner, 16th Biennal Conference on Carbon, San Diego/USA (1983)
[26] D. Brownbill, Modern Plastics International, March (1985)
[27] A.P. Cluley, SAMPE Conference, London (1983), Paper 5
[28] K.J. Humphris, Shell Polymers 7, 1 (1983)
[29] E. Fitzer, G. Hartwig, H. Jaeger, International Conference on Carbon, Bordeaux/France (1984)
[30] G. Hartwig, H. Jäger, S. Knaak, ICMC, Nonmetallic Materials and Composites at Low Temperatures, Heidelberg/FRG (1984)
[31] I. Brewster, J.B. Cattanach, SAMPE Conference, London (1983), Paper 3
[32] F.N. Cogswell, M.S. Swerdlow, SAMPE Conference, Stresa (1982)
[33] G. Kempe, H. Krauss, 14th Congress International Council of Aeronautical Sciences, Toulouse/France (1984)
[34] J.T. Hartness, SAMPE Quarterly, Januar (1983)
[35] H. Krauss, G. Kempe, DFVLR Stuttgart, IB-435-18/83
[36] E. Fitzer, R. Weiss, German Society for Metallurgy, Konstanz/GDR (1981) VDI-Vkrlag
[37] E. Fitzer, R. Weiss, VDI-Tagung, Baden-Baden/FRG (1981), VDI-Verlag
[38] E. Fitzer, K.-H. Geigl, L.M. Manocha, 5th London Intern. Conference on Carbon and Graphite (1974)
[39] P. Ehrburger, J. Herques, J.B. Donnet, ACS-Symposium Series 21 (1976)
[40] Monsanto Research Corp., St. Louis/US P 3 627 570
[41] J. Cziollek, E. Fitzer, Conference Internationale sur les Carbones, Bordeaux/France (1984)
[42] MAN AG, DBP 163 071 (1971)
[43] J.B. Donnet, FP 7 211 897 (1972)
[44] Airforce, US P 3 671 411 (1972)
[45] E. Fitzer, R. Weiss, Int. Conference Interface-Interphase, Liège/Belgien (Okt. 1983)
[46] E. Fitzer, H. Jäger, 17th Biennal Conference on Carbon, Lexington/USA (1985)
[47] F.W. Crossman, W.J. Warren, P.C. Pinoli, Natl. SAMPE Symp. Exhib. (1976)
[48] G. Hartwig, ICMC, Nonmetallic Materials and Composites at Low Temperatures, Heidelberg/FRG (1984), HTHP, im Druck
[49] U.T. Kreibich, F. Lohse, R. Schmid, Nonmetallic Materials and Composites at Low Temperatures, Plenum Press, New York (1979)
[50] G. Hartwig, ICMC/ICEC Conference, San Diego/USA (1981)
[51] E. Fitzer, G. Hannes, H. Jäger, ICMC, Nonmetallic Materials and Composites at Low Temperatures, Heidelberg/FRG (1984), HTHP, in press
[52] H. Jaeger, Promotions-Arbeit, University of Karlsruhe, Institute for Chemical Technology (1985)
[53] E. Fitzer, H. Jäger, HTHP (1986), in press
[54] E. Fitzer, G. Hartwig, R. Weiss, HTHP 15 (1983)
[55] E. Fitzer, H. Jäger, ACS-Symposium, Carbon and other High Performance Fibres', Miami Beach/USA (1985), Composites, im Druck
[56] E. Fitzer, H. Jäger, Zeitschrift für Werkstofftechnik 16 und 17 (1985)
[57] E. Fitzer, H. Jäger, R. Weiss, 16th Conference on Carbon, San Diego/USA (1983)
[58] E. Fitzer, H. Jaeger, Working group on carbon, Spring Meeting, Karlsruhe Reports of the DGK, in press
[59] R.M. Ogorkiewicz, Composites, March (1971)
[60] J. Cziollek, E. Fitzer, G. Hannes, International Conference on Carbon, Bordeaux/France (1984)

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